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(54) Title: COMPOSITIONS AND METHODS FOR CHEMICAL-MECHANICAL PLANARIZATION OF NOBLE-METAL-FEATURED SUBSTRATES. THESE TREATED SUBSTRATES

(57) Abstract: A composition for chemical-mechanical planarization comprises periodic acid and an abrasive present in a combined amount sufficient to planarize a substrate surface having a feature thereon comprising a noble metal, noble metal alloy, noble metal oxide, or any combination thereof. In one embodiment, the periodic acid is present in an amount in a range of from about 0.05 to about 0.3 moles/kilogram, and the abrasive is present in an amount in a range of from about 0.2 to about 6 weight percent. In another embodiment, the composition further comprises a pH-adjusting agent present in an amount sufficient to cause the pH of the composition to be in a range of from about pH 5 to about pH 10, or of from about pH 1 to about pH 4. A method for planarizing a substrate surface having a feature thereon comprising at least one noble metal, noble metal alloy, or noble metal oxide, or a combination thereof, comprises providing a composition or slurry comprising periodic acid and an abrasive in a combined amount sufficient to planarize the substrate surface, and polishing the surface with the slurry. A substrate produced by such a method is also provided.

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COMPOSITIONS AND METHODS FOR CHEMICAL-MECHANICAL PLANARIZATION OF NOBLE-METAL-
FEATURED SUBSTRATES. THESE TREATED SUBSTRATES

BACKGROUND

Field of the Invention

[0001] The present invention relates generally to compositions for chemical-mechanical planarization, and more particularly to compositions for chemical-mechanical planarization of substrates ("noble-metal-featured substrates") having surface features comprising noble metals, noble metal alloys, noble metal oxides, and combinations thereof, associated methods, and substrates produced by such methods.

Description of Related Art

[0002] Chemical-Mechanical Planarization (also referred to as Chemical-Mechanical Polishing), or CMP, is commonly used in the manufacture of semiconductor devices and denotes the process of removing material and forming a substantially planar surface before additional layers are deposited and/or additional patterning of the layers occurs. CMP processes have been extensively studied for use in semiconductor fabrication and constitute integral steps in many practical production environments. However, CMP of metals has been studied most extensively in connection with metals such as tungsten, copper, aluminum, tantalum, among others, as well as oxides, nitrides and alloys thereof. See, for example, Chemical Mechanical Planarization of Microelectronic Materials, by J. M. Steigerwald, S. P. Murarka and R. J. Gutmann (John Wiley & Sons 1997), especially Chapters 5 – 8. In contrast, CMP of noble metals, including alloys and oxides thereof, is much less well studied. The term "noble metals" typically refers to less reactive metals such as gold, silver, platinum, iridium and other elements typically found in or near Group VIII of the periodic table.

[0003] Interest in noble metals, and the alloys and oxides thereof, is increasing as such materials are useful as electrode and barrier materials in the fabrication of some electronic devices such as Gigabit (10^9 bit) DRAMs (dynamic random access memories) and FeRAMs (ferroelectric random access memories). Worldwide efforts are underway

to commercialize high dielectric constant and ferroelectric thin films for use in capacitive elements as would be applied, for example, in advanced DRAMs and FeRAMs. High dielectric constant materials such as BaSrTiO_3 (BST) can be used for forming capacitor dielectrics in submicron integrated circuits (e. g. in DRAM storage capacitors, coupling capacitors in general circuits, among other uses). Additionally, ferroelectric materials such as PbZrTiO_3 (PZT) and $\text{SrBi}_2\text{Ti}_2\text{O}_9$ that can store charge for extended periods of time can be employed in the fabrication of non-volatile FeRAM memory elements. The chemical properties of these (and other) high dielectric constant and ferroelectric materials typically require that they be used in conjunction with noble metals, noble metal oxides and/or noble metal alloys (including Pt, Ir, IrO_2 , among others). Examples of the use of high dielectric constant and/or ferroelectric materials in semiconductor fabrication and in conjunction with noble metals, noble metal alloys, and noble metal oxides, can be found in the following U.S. Patents: 5,318,927; 5,527,423; 5,976,928; 6,169,305, and references cited therein.

[0004] Conventional patterning of noble metals, noble metal alloys, and noble metal oxides includes the use of dry etching processes. However, dry etching has several disadvantages including unfavorable taper angle, fence formation, and a tendency to produce residual particles leading to contamination. Some of these disadvantages of conventional dry etching are due to the predominantly physical rather than chemical mechanism for material removal. Physical removal of material is prone to the formation of unwanted structures at the edges of the structures, such as electrodes, being etched.

SUMMARY

[0005] The present invention provides compositions and processes for the chemical-mechanical planarization or polishing (CMP) of substrates having at least one surface feature or layer comprising a noble metal, a noble metal alloy, and/or a noble metal oxide, or any combination thereof (sometimes referred to herein as noble metal features or the like). Suitable noble metals, noble metal alloys, and/or noble metal oxides include metals from Group VIII of the periodic table and include in particular, Pt, Ir and IrO_2 . Many of the noble-metal-containing substrate features contemplated are on the order of from about 300 Angstroms (A) to about 1000 A thick. The compositions and processes of the present invention are suitable for use in applications such as the polishing of these featured substrate surfaces at desirable polishing rates using standard CMP equipment. In

such applications, a suitable polishing rate may be from about 300 Angstroms per minute (A/min) to about 2000 A/min, merely by way of example.

[0006] As used herein, the chemical-mechanical planarization or polishing of a substrate having a metal feature or layer on its surface refers to the polishing of the substrate surface until the metal feature or layer is substantially coplanar with surrounding material, such as surrounding dielectric material, on the substrate. That is, the polishing of the metal-featured substrate continues until any metal excess is sufficiently removed to provide a substantially uniform profile across the substrate surface. By way of example, suitable surface uniformity (typically measured using known wafer profiling techniques) is reflected by wafer-within-wafer non-uniformity (WWNU) values of less than about 12%, preferably from about 4% to about 6%, or wafer-to-wafer non-uniformity (WTWNU) values of less than about 5%, preferably about 3%. Typically, each fabrication lab has acceptable uniformity values for each CMP process it uses, and generally prefers lower WWNU values or WTWNU values that indicate greater surface uniformity.

[0007] Preferably, the selectivity of the CMP composition used in this planarization or polishing process is high (at least greater than 1:1) in terms of the removal of metal relative to the removal of surrounding material or dielectric, where suitable selectivity ranges or values depend very much on the type of surrounding material or dielectric. By way of example, suitable selectivity ratios (i.e., removal of metal to removal of surrounding material or dielectric) may be on the order of 100:1 for tetraethoxysilane (TEOS) and 20:1 for boron phosphorous silicate glass (BPSG), though suitable ratios may be higher or lower than these particular ratios.

[0008] Once the metal feature is substantially coplanar with surrounding material on the substrate surface, further polishing may take place. Preferably, the selectivity ratio of the CMP composition used in this further polishing process is close to 1:1, such that dishing and erosion of the metal feature and the surrounding material is avoided or minimized. Typically, each fabrication lab has standards of acceptable dishing and erosion for the polished wafers (typically measured using wafer profiling techniques), and generally prefers lower levels of dishing and erosion that indicate greater surface quality.

[0009] An exemplary embodiment of the present invention is a composition for chemical-mechanical planarization that comprises periodic acid and an abrasive, wherein

the periodic acid and the abrasive are present in a combined amount that is sufficient to planarize a substrate surface having at least one feature or layer thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof. In an embodiment of the composition of the present invention, the periodic acid is present in an amount in a range of from about 0.05 to about 0.3 moles / kilogram, or preferably, from about 0.075 to about 0.175 moles/kilogram, and the abrasive is present in an amount in a range of from about 0.2 to about 6 weight percent, or preferably, from about 0.2 to about 4 weight percent.

[0010] The abrasive component of the composition may be an abrasive material having a Mohs hardness number of greater than about 6.5. For example, the abrasive may be one or more of alumina, silica, zirconia, spinel, zirconium nitride, and carbide. In an embodiment of the composition of the invention, the abrasive comprises alumina. By way of example, the alumina may be an alpha-alumina, a gamma-alumina, or a combination thereof.

[0011] In other embodiments, the composition or slurry comprises a pH-adjusting agent or titration agent in an amount sufficient to cause the pH level of the slurry to be in a desirable range. In various embodiments the pH range is from about pH 5 to about pH 10, preferably, from about pH 7 to about pH 9, or from about pH 1 to about pH 4, preferably from about pH 2 to about pH 3. Suitable pH-adjusting agents include one or more of a quaternary amine and an inorganic base, such as tetramethylammonium hydroxide, ammonium hydroxide, potassium hydroxide, and sodium hydroxide. In still another embodiment, the composition further comprises a suspension agent, which is preferably a surfactant.

[0012] An exemplary embodiment of a method of the present invention for planarizing a substrate surface having at least one feature or layer thereon comprising at least one noble metal, noble metal alloy, or noble metal oxide, or any combination thereof. The method comprises providing a composition or slurry comprising periodic acid and an abrasive present in a combined amount that is sufficient to planarize the substrate surface, and polishing the surface with the slurry. In an embodiment of the method, the periodic acid is present in an amount in a range of from about 0.05 to about 0.3 moles/kilogram, or preferably, from about 0.075 to about 0.175 moles/kilogram, and the abrasive is present in an amount in a range of from about 0.2 to about 6 weight percent, or preferably, from

about 0.2 to about 4 weight percent. In another embodiment of the method of the invention, the abrasive comprises an abrasive material discussed above, for example, alumina, whether alpha-alumina, gamma-alumina, or a combination thereof. In other embodiments, the slurry comprises a pH-adjusting agent or titration agent, also as described above, such that the pH level of the slurry is in a desirable range.

[0013] Use of the compositions and processes of the present invention may reduce, minimize or eliminate imperfections, defects, corrosion, recession and/or erosion that might otherwise appear on the substrate surfaces. Merely by way of example, the compositions and processes of the present invention may be used to meet objectives such as providing metal-featured substrates, such as Ir- or IrO₂-featured substrates, that have a surface roughness of less than about 4 Å and that are substantially corrosion-free, or providing metal-featured substrates that have dishing and erosion values of much less than 1000 Å, such as less than about 500Å, for example, about 300Å.

[0014] The present invention further encompasses a substrate produced by the methods disclosed herein. According to various embodiments of the invention, the substrate is substantially planar following chemical-mechanical polishing, has a WWNU of less than about 12%, and/or has a WTWNU of less than about 5%.

DETAILED DESCRIPTION

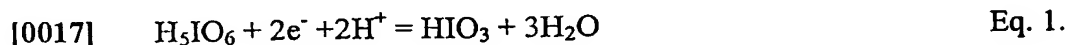
[0015] Compositions, associated methods, and substrates produced by such methods, according to the present invention are set forth in this description. In the examples set forth below, all numerical values and ranges are approximate unless explicitly stated otherwise.

Ir Polishing Compositions

Composition A

[0001] A polishing composition (such as "Composition A") useful for polishing iridium pursuant to some embodiments of the present invention is comprised of an abrasive (typically an alumina) and periodic acid (H₅IO₆) in aqueous solution (advantageously in distilled or di-ionized water, referred to collectively herein as "DI" water). Periodic acid is capable of participating in a fairly complex group of chemical reactions. Periodic acid is a rather weak acid ($K_a \approx 5.1 \times 10^{-5}$) and a strong oxidizing agent under acidic

conditions ($E^{\circ} = 1.6 \text{ V}$). Depending on the pH of the medium containing periodic acid, different reactive species can be called into play including H_5IO_6 , H^+ , H_4IO_6^- , IO_4^- , $\text{H}_3\text{IO}_6^{2-}$. During the short contact time in typical CMP processing, the primary periodic acid reaction is thought to be that represented below in Equation 1 (Eq. 1).



[0018] The reaction represented in Equation 1 is believed to be the primary CMP reaction involving periodic acid, although additional or different reactions may participate within the scope of the present invention.

[0019] Various CMP compositions are described herein in terms of the reactants and other chemical components that are mixed or otherwise combined to form the desired CMP slurry. However, it is recognized that a complex set of chemical processes typically follows blending of the CMP components that may destroy or alter, entirely or in part, one or more of the blended components. The CMP solutions comprising some embodiments of the present invention are described herein in terms of the blended components, with the understanding that the chemical composition (or range of compositions) of the resulting CMP slurry is the necessary result of chemical processes occurring between and among the blended components under the conditions specified. Thus, descriptions herein of the components blended to form a CMP slurry are intended to encompass the chemical species resulting from such blending under the condition (or set of conditions) specified.

[0020] One example of component concentrations for Composition A is shown in the following Table I.

Composition A Component Concentration

Table I: Typical Composition A

Component	Component Concentration
Alumina Abrasive	2 weight % ("wt %")
Periodic Acid	0.1 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition A

[0021] Thus, for example, a 10 kilogram mixture of Composition A may be prepared by combining 200 grams of an alumina (whether alpha-, gamma-, or a combination of alpha- and gamma-alumina) abrasive, 1 mole of periodic acid and the remaining of amount DI water. One form of alpha-alumina abrasive advantageously used in connection with some compositions herein is the commercial product "CR-30" manufactured by Baikowski Chimie Co. of Annacey Cedex 9, France. Other sources of alpha-alumina, as well as sources of gamma-alumina or alpha- and gamma-alumina, may also be utilized.

pH Ranges

[0022] Composition A typically has a pH range from about 1 to about 2.5, and favorably (in terms of performance), a pH of about 1.5.

Preparation

[0023] Generally, Composition A is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and subsequently adding the periodic acid (H_5IO_6). The composition is typically stirred continuously within the container during at least the time of the preparation of the composition.

CMP Process

[0024] A typical example of the mixing ratio, process, pH and removal rate associated with Composition A is set forth in Table A, in which "A/min" denotes Angstroms (10^{-10} meter) of material removed per minute of processing.

Mixing Ratio, Process, pH and Removal Rate

Table A

Mixing Ratio	Process	pH	Ir Removal Rate (A/min)
2 wt % Alpha-Alumina Abrasive	4/0/50/51/150	1.5 – 2.5	288
0.1 mol/l kg Periodic Acid			
DI Water			

[0025] In the example of Table A, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed of 51 rpm, and a composition flow rate of 150 ml/min.

A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as the buff pad on the secondary platen of the polisher. Composition A was stirred thoroughly before and during its use.

[0026] When employed according to the process of Table A, Composition A provided an Ir removal rate of approximately 288 Angstroms per minute. Additionally, Composition A provided an Ir removal rate of approximately 375 Angstroms per minute when carried out according to the above-described process (as set forth in Table A) with one variation, namely, applying a higher down force pressure of 6 psi. Furthermore, Composition A provided an Ir removal rate of approximately 400 Angstroms per minute when carried out according to the process set forth in Table A with one variation, namely, applying a higher table speed of 70 rpm. Generally, high removal rates (in terms of the material targeted for removal) are preferred.

Ir Polishing Compositions Including Titration with TMAH

Composition B

[0027] Other Ir polishing compositions (such as "Composition B") pursuant to some embodiments of the present invention comprise an alumina abrasive (alpha-, gamma-, or both), periodic acid (H_5IO_6), DI water, and a pH-adjusting agent, or a base, typically tetramethylammonium hydroxide (TMAH). One example of component concentrations for Composition B is shown in Table II.

Composition B Component Concentration

Table II: Typical Composition B

Component	Component Concentration
Alpha-Alumina Abrasive	2 wt %
Periodic Acid	0.1 mol/kg
DI Water	Remaining weight amount to obtain final desired amount of Composition B
Tetramethylammonium Hydroxide (TMAH)	Titrate with TMAH to a pH of approximately between 6 and 7

[0028] By way of example, a 10 kilogram mixture of Composition B may be prepared by combining 200 grams of an alumina abrasive, 1 mole of periodic acid and the remaining amount of DI water. This mixture is then titrated with the titration agent TMAH to obtain a final pH of about 6 to about 7.

pH Ranges

[0029] Composition B typically has a pH range from about 6 to about 7 and, advantageously (in terms of performance), a pH of about 7.

Preparation

[0030] Generally, Composition B is prepared by adding the alumina abrasive to a container of DI water and subsequently adding the periodic acid (H_5IO_6). This mixture is then titrated with TMAH to obtain a final pH value of about 6 to about 7. Composition B is advantageously continuously stirred within the container during at least the period of composition preparation.

CMP Process

[0031] An example of the mixing ratio, process, pH and removal rate associated with Composition B is set forth in Table B.

Mixing Ratio, Process, pH and Removal Rate

Table B

Mixing Ratio	Process	pH	Ir Removal Rate (A/min)
2 wt % Alpha-Alumina Abrasive	4/0/50/5	6 - 7	325
0.1 mol/1 kg Periodic Acid	1/150		
DI Water			
Titrate with TMAH to a pH of approximately 7			

[0032] In the example of Table B, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed 51 rpm, and a composition flow rate of 150 ml/min. A

stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen, and a Polytex pad was used as the buff pad on the secondary platen. Composition B was stirred thoroughly before and during its use.

[0033] When employed according to the above-described process, Composition B provided an Ir removal rate of approximately 325 Angstroms per minute.

Ir Polishing Compositions Including Titration with NH_4OH

Composition C

[0034] Other Ir polishing compositions (such as "Composition C") pursuant to some embodiments of the present invention are comprised of an alumina (alpha-, gamma-, or both) abrasive, periodic acid (H_5IO_6), DI water, and a pH-adjusting agent or a base, such as ammonium hydroxide (NH_4OH). One example of component concentrations for Composition C is shown below in Table III.

Composition C Component Concentration

Table III: Typical Composition C

Component	Component Concentration
Alpha-Alumina Abrasive	2 wt %
Periodic Acid	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition C
Ammonium Hydroxide (NH_4OH)	Titrate with NH_4OH to a pH of approximately 7

[0035] By way of example, 200 grams of an alumina abrasive, 1 mole of periodic acid and the remaining amount of DI water may be combined to provide a 10 kilogram mixture of Composition C. This mixture is then titrated with titration agent NH_4OH to obtain a final pH of about 6 to about 7.

pH Ranges

[0036] Composition C typically has a pH range from about 6 to about 7 and a favorable pH of about 7.

Preparation

[0037] Generally, Composition C is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and subsequently adding the periodic acid (H_5IO_6). This mixture is then titrated with the titration agent NH_4OH to obtain a final pH value of about 7. Composition C is advantageously stirred continuously within the container during at least the period of composition preparation.

CMP Process

[0038] An example of the mixing ratio, process, pH, removal rate and selectivity associated with Composition C is set forth in Table C.

Mixing Ratio, Process, pH, Removal Rate, and SelectivityTable C

Mixing Ratio	Process	pH	Ir Removal Rate (Å/min)	Ir:TEOS Selectivity
2 wt % Alpha-Alumina Abrasive 0.1 mol/l kg Periodic Acid Remaining % DI Water Titrate with NH_4OH to a pH of approximately 7	5/0/90/50/150	6 - 7	360	1.8:1

[0039] In the example of Table C, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 5 psi, a back pressure of 0 psi, a table speed of 90 rpm, a carrier speed 50 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen, and a Polytex pad was used as the buff pad on the secondary platen. Composition C was stirred thoroughly before and during its use.

[0040] When employed according to the process of Table C, Composition C provided an Ir removal rate of approximately 360 Angstroms per minute. The Ir removal rates were compared with tetrathoxysilane (TEOS) removal rates, yielding a Ir:TEOS selectivity of 1.8:1. Generally speaking, high selectivity ratios (in terms of the material targeted for

removal to another material) are preferred.

Composition D

[0041] According to some embodiments of the present invention, other Ir polishing compositions (such as "Composition D") are comprised of an alumina (alpha-, gamma-, or both) abrasive, periodic acid (H_5IO_6), DI water and a pH-adjusting agent or base such as ammonium hydroxide (NH_4OH). Illustrative component concentrations for Composition D are shown in the following Table IV.

Composition D Component Concentration

Table IV: Typical Composition D

Component	Component Concentration
Alpha-Alumina Abrasive	2 wt %
Periodic Acid	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition D
Ammonium Hydroxide (NH_4OH)	Titrate with NH_4OH to a pH of approximately 3

[0042] By way of example, 200 grams of alumina abrasive, 1 mole of periodic acid and the remaining amount DI water may be combined to provide a 10 kilogram mixture of Composition D. This mixture is then titrated with titration agent NH_4OH to obtain a final pH of about 3.

pH Ranges

[0043] Composition D typically has a pH range from about 2 to about 4 and a favorable pH value of about 3.

Preparation

[0044] Generally, Composition D is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and subsequently adding the periodic acid (H_5IO_6). This mixture is then titrated with NH_4OH to obtain a final pH value of about 3. Composition D is favorably continuously stirred within the container during at least the

time of composition preparation.

CMP Process

[0045] One example of the mixing ratio, process, pH, removal rate and Ir:TEOS selectivity associated with Composition D is set forth in Table D.

Mixing Ratio, Process, pH, Removal Rate and Selectivity

Table D

Mixing Ratio	Process	pH	Ir Removal Rate (Å/min)	Ir:TEOS Selectivity
2 wt % Alpha-Alumina Abrasive 0.1 mol/l kg Periodic Acid Remaining % DI Water Titrate with NH ₄ OH to a pH of approximately 3	5/0/90/50/150	3 - 4	320	1:1.5

[0046] In the example set forth in Table D, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 5 psi, a back pressure of 0 psi, a table speed of 90 rpm, a carrier speed 50 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen, and a Polytex pad was used as the buff pad on the secondary platen. Composition D was stirred thoroughly before and during its use.

[0047] When employed according to the above-described process (as set forth in Table D), Composition D provided an Ir removal rate of approximately 320 Angstroms per minute. The Ir removal rates were compared with tetraethoxysilane (TEOS) removal rates, yielding a Ir:TEOS selectivity of 1:1.5.

Ir Polishing Compositions including Suspension Agents

[0048] Other examples of Ir polishing compositions pursuant to some embodiments of the present invention comprise one or more agents for making an improved suspension. Typically such suspension-improving agents (hereinafter, "suspension agents") include

abrasives.

Composition E

[0049] For example, some such Ir polishing compositions (such as "Composition E") comprise the components of Composition D and a second abrasive as a suspension agent. By way of example, in some such Ir polishing compositions the second abrasive may be Alumina-C as a 15% suspension. Alumina-C is a product, Aluminumoxid C (CAS#1344-28-1), of Deguss-Huls AG, which is used to keep the slurry in suspension for a suitable, and preferably long period. One example of component concentrations for Composition E is set forth in Table V.

Composition E Component Concentration

Table V: Typical Composition E

Component	Component Concentration
Alpha-Alumina Abrasive	2 wt %
Periodic Acid	0.1 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition E
Ammonium Hydroxide (NH ₄ OH)	Titrate with NH ₄ OH to a pH of approximately 3
Alumina-C (15% suspension)	0.9 wt %

pH Ranges

[0050] Composition E typically has a pH range from about 2 to about 4 and, advantageously, a pH of about 3.

Preparation

[0051] Generally, Composition E is prepared by adding the alpha-alumina abrasive (such as CR-30) to a container of DI water and subsequently adding the periodic acid (H₅IO₆). This mixture is then titrated with NH₄OH to obtain a final pH value of about 3. Finally, the second abrasive is added. Continuous stirring is maintained during at least the period

of composition preparation.

CMP Process

[0052] An example of the mixing ratio, process, pH, removal rate and selectivity associated with Composition E is set forth in Table E.

Mixing Ratio, Process, pH, Removal Rate, and Selectivity

Table E

Mixing Ratio	Process	pH	Ir Removal Rate (Å/min)	Ir:TEOS Selectivity
2 wt % Alpha-Alumina Abrasive	5/0/90/50/150	3 - 4	260	1:2.2
0.1 mol/l kg Periodic Acid				
Remaining % DI Water				
Titrate with NH ₄ OH to a pH of approximately 3				
0.9 wt % Second Abrasive (e.g., Alumina-C)				

[0053] In the example set forth in Table E, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 5 psi, a back pressure of 0 psi, a table speed of 90 rpm, a carrier speed of 50 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as polishing pad on the primary platen, and a Polytex pad was used as the buff pad on the secondary platen. Composition E was stirred thoroughly before and during its use.

[0054] When employed according to the process of Table E, Composition E provided an Ir removal rate of approximately 260 Angstroms per minute. The Ir removal rates were compared with tetraethoxysilane (TEOS) removal rates, yielding a Ir:TEOS selectivity of 1:2.2.

Composition F

[0055] Other Ir polishing compositions (such as "Composition F") pursuant to the some

embodiments of the present invention comprise the components of Composition C and a second abrasive as a suspension agent. In one such composition, a slurry suspension agent, Laponite (a product of Southwestern Clay Co. of Gonzales, Texas) was used. Laponite is typically hydrous sodium lithium magnesium fluoro-silicate (Laponite B), hydrous sodium lithium magnesium silicate (Laponite D, RD, ED, HB, G, XLG), hydrous sodium lithium magnesium silicate modified with tetra sodium pyrophosphate (Laponite DS, RDS, XLS, S, JS, MS), or hydrous sodium lithium magnesium silicate treated to give a fluoride loading of 2000 ppm (Laponite DF). Although any of the types of Laponite can be used with comparable results, Laponite B was used in the example described below.

[0056] One example of component concentrations for Composition F is shown in Table VI.

Composition F Component Concentration

Table VI: Typical Composition F

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/l kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	8 grams
Laponite (Second Abrasive)	0.5 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %) (First Abrasive)	12.5 grams, or about 2 wt %

Preparation

[0057] In one example, Composition F is prepared by combining an "Oxidizer A", described below, and an "Abrasive A", also described below. In the preparation of Oxidizer A, the periodic acid (H₅IO₆) is added to a container of DI water (76 grams). This mixture is then titrated with pH-adjusting agent or titration agent NH₄OH to a final

pH value of about 7. This resultant mixture is referred to herein as Oxidizer A. Abrasive A is prepared by adding the Laponite and the alumina abrasive to eight grams of DI water. Oxidizer A is added to Abrasive A to produce Composition F. Continuous stirring is maintained during at least the period of composition preparation.

Composition G

[0058] Other Ir polishing compositions (such as "Composition G") pursuant to some embodiments of the present invention comprise the components of Composition C and a slurry suspension agent, such as the surfactant Darvan C. Darvan C is a commercial ammonium polymethacrylate aqueous solution sold by R. T. Vanderbilt Company, Inc. of Norwalk, CT.

[0059] One example of component concentrations for Composition G is set forth in Table VII.

Composition G Component Concentration

Table VII: Typical Composition G

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/l kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	8 grams
Darvan C	0.5 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %) (First Abrasive)	12.5 grams, or about 2 wt %

Preparation

[0060] In one example, Composition G is prepared by combining Oxidizer A and "Abrasive B", as described below. Oxidizer A is prepared as previously described in relation to Composition F. Abrasive B is prepared by adding the Darvan C and the alumina abrasive to eight grams of DI water. Oxidizer A is added to Abrasive B to

produce Composition G. Continuous stirring is maintained during the composition preparation.

Composition H

[0061] Other Ir polishing compositions (such as "Composition H") pursuant to some embodiments of the present invention comprise the components of Composition C and a second abrasive as a suspension agent. In some embodiments, the second abrasive is LUDOX TM-50. LUDOX TM-50 is a commercial colloidal silica abrasive of E. I. Du Pont de Nemours and Company, having advantageous properties in terms of particle size and contribution to composition suspension and stability.

[0062] One example of component concentrations for Composition H is set forth in Table VIII.

Composition H Component Concentration

Table VIII: Typical Composition H

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/l kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	8 grams
LUDOX TM-50 (Second Abrasive)	0.5 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %) (First Abrasive)	12.5 grams, or about 2 wt %

Preparation

[0063] Generally, Composition H is prepared by combining Oxidizer A and "Abrasive C", as described below. Oxidizer A is prepared as previously described. Abrasive C is prepared by adding the LUDOX TM-50 (the second abrasive) and the alumina abrasive (the first abrasive) to eight grams of DI water. Oxidizer A is added to Abrasive C to

produce Composition H. Continuous stirring is maintained during at least the composition preparation.

Composition I

[0064] Other Ir polishing compositions (such as "Composition I") pursuant to some embodiments of the present invention comprise the components of Composition C and a slurry suspension agent. In some embodiments, the suspension agent is ethyl carbonate. One example of component concentrations for Composition I is set forth in Table IX.

Composition I Component Concentration

Table IX: Typical Composition I

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/l kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	8 grams
Ethyl Carbonate	0.5 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %)	12.5 grams, or about 2 wt %

Preparation

[0065] In one example, Composition I is prepared by combining Oxidizer A and "Abrasive D", as described below. Oxidizer A is prepared as previously described. Abrasive D is prepared by adding the ethyl carbonate and the alumina abrasive to eight grams of DI water. Oxidizer A is added to Abrasive D to produce Composition I. Continuous stirring is maintained during the composition preparation.

Composition J

[0066] Other Ir polishing compositions (such as "Composition J") pursuant to some embodiments of the present invention comprise the components of Composition C and an organic acid as a suspension agent. In one embodiment, the organic acid is succinic acid.

In other embodiments, alternative water soluble organic acids (e.g. mono-, di-, and tri-functional acids) can be used, as can other suspension agents or surfactants that act to suspend the abrasive. One example of component concentrations for Composition J is set forth in Table X.

Composition J Component Concentration

Table X: Typical Composition J

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/1 kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	7.5 grams
Succinic acid	1.0 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %)	12.5 grams, or about 2 wt %

Preparation

[0067] In one example, Composition J is prepared by combining Oxidizer A and "Abrasive E". Oxidizer A is prepared as previously described. Abrasive E is prepared by adding the succinic acid (as an exemplary organic acid) and the alumina abrasive to 7.5 grams of DI water. Oxidizer A is added to Abrasive E to produce Composition J. Continuous stirring is maintained during the composition preparation.

Composition K

[0068] Other Ir polishing compositions (such as "Composition K") pursuant to the present invention comprise the components of Composition C and a second abrasive as a suspension agent. In some embodiments, the second abrasive is an alumina abrasive in the form of "CR-140". Cr-140 is a commercial abrasive product manufactured by Baikowski Chimie Co. of Annacey Cedex 9, France, believed to comprise about 95% gamma-alumina and about 5% alpha-alumina. One example of component concentrations for Composition K is set forth in the Table XI.

Composition K Component ConcentrationTable XI: Typical Composition K

Component	Component Concentration
Periodic Acid	2.3 grams, or 0.1 mol/l kg
DI Water	76 grams
Ammonium Hydroxide (NH ₄ OH)	Titrate the above components with NH ₄ OH to a pH of approximately 7
DI Water	3.5 grams
CR-140 @ 20 wt % (Second Abrasive)	5.0 grams
Alpha-Alumina Abrasive (CR-30 @ 16 wt %) (First Abrasive)	12.5 grams, or about 2 wt %

Preparation

[0069] In one example, Composition K is prepared by combining Oxidizer A (prepared as previously described) and "Abrasive F". Abrasive F is prepared by adding CR-140 (the second abrasive) and CR-30 (the first abrasive) to 3.5 grams of DI water. Oxidizer A is added to Abrasive F to produce Composition K. Continuous stirring is maintained during the composition preparation.

[0070] Preparation conditions associated with Compositions F through K are set forth below in Table 1.

Compositions F Through K Preparation ConditionsTable 1

Composition	DI Water	Second Abrasive	First Abrasive	Stir Time	Oxidizer	Stir Time
Composition F	8 grams	0.5 grams Laponite	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.
Composition G	8 grams	0.5 grams Darvan C	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.
Composition H	8 grams	0.5 grams LUDOX TM-50	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.
Composition I	8 grams	0.5 grams Ethyl Carbonate	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.
Composition J	7.5 grams	1.0 grams Succinic acid	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.
Composition K	3.5 grams	5 grams CR-140 (20% wt)	12.5 grams, or about 2 wt %	2 hours	79 grams of Oxidizer A	> 20 min.

[0071] Table 2 below sets forth the pH, settling time, Ir removal rate and Ir:TEOS selectivity associated with Compositions F through K. As used herein, settling time refers to the time it takes for a homogenous slurry mixture to settle in an ambient environment so that a clear top layer is formed. In these examples, the unit of measure for settling time is millimeters of clear liquid (i.e., the depth of the clear top layer measured from the top of the original homogenous mixture) in a given unit of time. For instance, a settling time of 9 mm/10 min indicates that a 9 mm deep layer of clear liquid was formed after 10 minutes of standing in an ambient environment. Generally, a suitable slurry, such as any of the examples of Compositions F through K, should not settle in a relatively "hard" or packed manner such that the slurry can't be resuspended with minimal agitation.

[0072] For Ir polishing, Composition H is preferred in view of its favorable Ir removal rate of 240 A/min, and more particularly, its favorable 3.9:1 Ir:TEOS selectivity, which relatively high selectivity is believed to play an important role at the end of the polishing step.

pH, Settling Time, Ir Removal Rate and Selectivity for Compositions F Through K**Table 2**

Composition	pH	Settling Time (mm/min)	Ir Removal Rate (A/min)	Ir:TEOS Selectivity
Composition F	7.3	9 mm/10 min	240	2.7:1
Composition G	7.3	9 mm/10 min	340	2.1:1
Composition H	7.3	9 mm/10 min	240	3.9:1
Composition I	7.3	9 mm/10 min	350	2.3:1
Composition J	6.7	5 mm/2 hrs	80	1:1.3
Composition K	6.9	10 mm/10 min	230	3.4:1

[0073] Each of the CMP processes set forth in Table 2 above was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Compositions F through K were stirred thoroughly before and during their use.

IrO₂ Polishing Compositions**Composition L (for polishing IrO₂)**

[0074] Iridium oxide (IrO₂) polishing compositions (such as "Composition L") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, hydrazine hydrate (NH₂-NH₂-H₂O), and DI water. Hydrazine hydrate is believed to contribute to the polishing of the noble metal oxide. Further, it is believed that the caustic hydrazine hydrate may also serve as a reducing agent, although this effect may be slight or minimal. According to the present invention, an IrO₂ polishing composition should have a pH of from about pH 5 to about pH 10, preferably, from about pH 7 to about pH 9. An example of component concentrations for Composition L is set forth below in Table XII.

Composition L Component ConcentrationTable XII: Typical Composition L

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Hydrazine hydrate	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition L

pH Ranges

[0075] Composition L typically has pH level of pH 8 or greater, such as from about pH 8 to about pH 10 and, advantageously, from about pH 9 to about pH 9.5.

Preparation

[0076] Generally, Composition L is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and subsequently adding the hydrazine hydrate. Composition L is typically continuously stirred within the container during at least the period of composition preparation.

CMP Process

[0077] An example of the mixing ratio, process, pH and removal rate associated with Composition L is set forth below in Table L.

Mixing Ratio, Process, pH and Removal RateTable L

Mixing Ratio	Process	pH	IrO ₂ Removal Rate (A/min)
2 wt % Alpha-Alumina Abrasive	4/0/50/51/150	9-9.5	880
0.1 mol/1 kg Hydrazine hydrate			
DI Water			

[0078] In the example set forth in Table L, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0

psi, a table speed of 50 rpm, a carrier speed 51 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as buff pad on the secondary platen of the polisher. Composition L was stirred thoroughly before and during its use.

[0079] When employed according to the process set forth in Table L, Composition L provided an IrO_2 removal rate of approximately 880 Angstroms per minute.

[0080] Another example of component concentrations for Composition L (denoted as "Composition L(a)") is shown below in Table XIIa.

Composition L(a) Component Concentration

Table XIIa: Typical Composition L(a) (additional embodiments)

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Hydrazine hydrate	0.05 mol/kg
DI Water	Remaining weight amount to obtain final desired amount of Composition L

pH Ranges

[0081] The example of Table XIIa has a favorable pH value of about 9.

CMP Process

[0082] An example of the mixing ratio, process, pH and removal rate associated with Composition L(a) is set forth below in Table L(a).

Mixing Ratio, Process, pH and Removal RateTable L(a)

Mixing Ratio	Process	pH	IrO ₂ Removal Rate (Å/min)
2 wt % Alpha-Alumina Abrasive 0.05 mol/l kg Hydrazine hydrate DI Water	4/0/50/51/150	9	740

[0083] In the example set forth in Table L(a), the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed of 51 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as buff pad on the secondary platen of the polisher. The above Composition L(a) was stirred thoroughly before and during its use.

[0084] When employed according to the process of Table L(a), Composition L(a) provided an IrO₂ removal rate of approximately 740 Angstroms per minute.

Composition M (for polishing IrO₂)

[0085] Other iridium oxide (IrO₂) polishing compositions (such as "Composition M") pursuant to some embodiments of the present invention are comprised of an alumina (alpha-, gamma, or both) abrasive, tetramethylammonium hydroxide (TMAH), and DI water. TMAH is believed to contribute to the polishing of the noble metal oxide. An example of component concentrations for Composition M is set forth below in Table XIII.

Composition M Component ConcentrationTable XIII: Typical Composition M

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Tetramethylammonium Hydroxide	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition M

pH Ranges

[0086] Composition M typically has a pH level of pH 8 or greater, such as in a range from about pH 9 to about pH 11 and, favorably, of about pH 10.

Preparation

[0087] Generally, Composition M is prepared by adding the alpha-alumina abrasive (CR-30) to a container of DI water and subsequently adding tetramethylammonium hydroxide (TMAH). Composition M is preferably continuously stirred within the container during at least the composition preparation.

CMP Process

[0088] An example of the mixing ratio, process, pH and removal rate associated with Composition M is set forth below in Table M. For IrO₂ polishing, Composition M is preferred in view of its favorable IrO₂ removal rate of 635 Å/min.

Mixing Ratio, Process, pH and Removal RateTable M

Mixing Ratio	Process	pH	IrO ₂ Removal Rate (Å/min)
2 wt % Alpha-Alumina Abrasive 0.1 mol/kg Tetramethylammonium Hydroxide DI Water	4/0/50/51/150	10	635

[0089] In the example set forth in Table M, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed of 51 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as buff pad on the secondary platen of the polisher. The Composition M of the example was stirred thoroughly before and during its use.

[0090] When employed according to the above process, Composition M provided an IrO_2 removal rate of approximately 635 Angstroms per minute.

[0091] Another example of component concentrations for Composition M (denoted herein as "Composition M(a)") is set forth below in Table XIIIa.

Composition M(a) Component Concentration

Table XIIIa: Typical Composition M(a)

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Tetramethylammonium Hydroxide	0.03 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition M

pH Ranges

[0092] Composition M(a) has an advantageous pH range from about 9 to about 10.

CMP Process

[0093] An example of the mixing ratio, process, pH and removal rate for Composition M(a) is set forth below in Table M(a).

Mixing Ratio, Process and Removal RateTable M(a)

Mixing Ratio	Process	pH	IrO ₂ Removal Rate (A/min)
2 wt % Alpha-Alumina Abrasive	4/0/50/51/150	9 - 10	320
0.03 mol/kg Tetramethylammonium Hydroxide			
DI water			

[0094] In the example set forth in Table M(a), the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed of 51 rpm, and a composition flow rate of 150 ml/min. A stacked pad of IC-1000 over a Suba IV was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as buff pad on the secondary platen of the polisher. The Composition M(a) of this example was stirred thoroughly before and during its use.

[0095] When employed according to the process of Table M(a), Composition M(a) provided an IrO₂ removal rate of approximately 320 Angstroms per minute.

Platinum (Pt) Polishing CompositionsComposition N

[0096] Platinum (Pt) polishing compositions (such as "Composition N") pursuant to some embodiments of the present invention comprise an alumina abrasive (alpha-, gamma-, or both), periodic acid (H₅IO₆), and DI water. Thus, Composition N is comprised of the same components as Composition A. An example of component concentrations for Composition N is set forth below in Table XIV.

Composition N Component ConcentrationTable XIV: Typical Composition N

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Periodic Acid	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition N

pH Ranges

[0097] Composition N advantageously has a pH value of about 1.6.

Preparation

[0098] Generally, Composition N is prepared by adding water the alumina abrasive (such as CR-30) to a container of DI and subsequently adding the periodic acid (H_5IO_6). Composition N is advantageously stirred continuously within the container during at least the period of composition preparation.

CMP Process

[0099] An example of the mixing ratio, process, pH, removal rates and selectivity associated with Composition N is set forth in Table N.

Mixing Ratio, Process, pH, Removal Rates, and SelectivityTable N

Mixing Ratio	Process	pH	Removal Rate (A/min) Pt	Removal Rate (A/min) BPSG	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasive	2/200/18/150	1.6	131	180	1:1.5
0.1 mol/l kg Periodic Acid					
DI water					

[00100] In the example set forth in Table N, the CMP process was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Composition N was stirred thoroughly before and during its use.

[00101] When employed according to the process of Table N, Composition N provides a Pt removal rate of 131 A/min and a Boron Phosphorous Silicate Glass (BPSG) removal rate of 180 A/min, demonstrating a Pt:BPSG selectivity of 1:1.5.

Composition O

[00102] Other platinum polishing compositions (such as "Composition O") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, periodic acid (H_5IO_6), ammonium chloride (NH_4Cl), and DI water. It is believed that the electrolyte, ammonium chloride, serves as a source of chloride ions that assist in metal etching. One example of component concentrations for Composition O is set forth below in Table XV.

Composition O Component Concentration

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Periodic Acid	0.1 mol/1 kg
Ammonium Chloride	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition O

pH Ranges

[00103] Composition O typically has a pH range from about 1.2 to about 1.8 and a favorable pH value of about 1.6.

Preparation

[00104] Generally, Composition O is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water, then adding the periodic acid (H_5IO_6), and then adding the ammonium chloride. Composition O is advantageously stirred continuously within the container during the composition preparation.

CMP Process

[00105] An example of the mixing ratio, process, pH, removal rates and selectivity for Composition O is set forth below in Table O.

Mixing Ratio, Process, pH, Removal Rates and SelectivityTable O

Mixing Ratio	Process	pH	Pt Removal Rate (A/min)	Removal Rate (A/min) BPSG	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasive	2/200/18/150	1.6	443	56	8:1
0.1 mol/kg Periodic Acid					
0.1 mol/kg Ammonium Chloride					
DI Water					

[00106] The CMP process of Table O for Composition O was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Composition O was stirred thoroughly before and during its use.

[00107] Composition O, when employed according to the process of Table O, Composition O provides a Pt removal rate of 443 A/min and a BPSG removal rate of 56 A/min, demonstrating a Pt:BPSG selectivity of 8:1.

Composition P

[00108] Other platinum polishing compositions (such as "Composition P") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, periodic acid (H_5IO_6), ammonium chloride (NH_4Cl), and DI water. One example of component concentrations for Composition P is set forth below in Table XVI.

Composition P Component ConcentrationTable XVI: Typical Composition P

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	6 wt %
Periodic Acid	0.1 mol/1 kg
Ammonium Chloride	0.1 wt %
DI Water	Remaining weight amount to obtain final desired amount of Composition P

pH Ranges

[00109] Composition P advantageously has a pH range from about 1.5 to about 2.

Preparation

[00110] Generally, Composition P is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water, then adding the periodic acid (H_5IO_6), and then adding the ammonium chloride (NH_4Cl). Composition P is favorably continuously stirred within the container during at least the composition preparation.

CMP Processes

[00111] Several examples of the processes and removal rates for Composition P are set forth below in Table P.

Processes and Removal RatesTable P

Process	Pt Removal Rate (A/min)
2/200/18/70	220
4/200/18/70	470
6/200/18/70	750
7/200/18/70	1,020

[00112] The CMP processes set forth in Table P were carried out using an IPEC 576

polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, 4 psi, 6 psi and 7 psi, respectively. All processes further employed a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 70 ml/min. Composition P was stirred thoroughly before and during its use.

[00113] When employed according to the processes set forth in Table P, Composition provides Pt removal rates of 220 A/min, 470 A/min, 750 A/min, and 1,020 A/min, respectively.

Composition Q

[00114] Other platinum polishing compositions (such as "Composition Q") pursuant to some embodiments of the present invention comprise an alumina abrasive (alpha-, gamma-, or both), ammonium chloride (NH_4Cl), and DI water.

Composition Q Component Concentration

Table XVII: Typical Composition Q

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Ammonium Chloride	0.1 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition Q

pH Ranges

[00115] The present Composition Q advantageously has a general pH range from about 5 to about 6 and a favorable pH of about 5.4.

Preparation

[00116] Generally, Composition Q is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and then adding the ammonium chloride. Composition Q is typically stirred continuously within the container during the composition preparation.

CMP Process

[00117] An example of the mixing ratio, process, pH, removal rates and selectivity associated with Composition Q is set forth below in Table Q. For Pt polishing, Composition Q is preferred in view of its favorable Pt removal rate of 1598 A/min and its favorable Pt:BPSG selectivity of 11:1.

Mixing Ratio, Process, pH, Removal Rates and Selectivity

Table Q

Mixing Ratio	Process	pH	Pt Removal Rate (A/min)	Removal Rate (A/min) BPSG	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasives	2/0/200/18/150	5.4	1598	145	11:1
0.1 mol/kg Ammonium Chloride					
DI Water					

[00118] The CMP process set forth in Table Q was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, a back pressure of 0 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Composition Q is advantageously stirred thoroughly before and during its use.

[00119] When employed according to the process of Table Q, Composition Q provides a Pt removal rate of 1,598 A/min and a BPSG removal rate of 145 A/min, demonstrating a Pt:BPSG selectivity of approximately 11:1.

Composition R

[00120] Other Pt polishing compositions (such as "Composition R") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, hydrochloric acid (HCl) and DI water. It is believed that the hydrochloric acid serves as a source of chloride ions that assist in the etching of metal. One example of component concentrations for Composition R is set forth below in Table XVIII.

Composition R Component ConcentrationTable XVIII: Typical Composition R

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Hydrochloric Acid	0.1 mol/kg
DI Water	Remaining weight amount to obtain final desired amount of Composition R

pH Ranges

[00121] Composition R typically has a pH range from about 1.0 to about 2.0 and a favorable pH of about 1.2.

Preparation

[00122] Generally, Composition R is prepared by adding the alumina abrasive (CR-30) to a container of DI water and subsequently adding the hydrochloric acid. Composition R is favorably continuously stirred within the container during at least the composition preparation.

CMP Process

[00123] An example of the mixing ratio, process, pH, removal rates and selectivity for Composition R is set forth below in Table R.

Mixing Ratio, Process, pH, Removal Rates and SelectivityTable R

Mixing Ratio	Process	pH	Pt Removal Rate (A/min)	BPSG Removal Rate (A/min)	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasive	2/0/200/18	1.2	334	26	13:1
0.1 mol/kg Hydrochloric Acid					
DI Water					

CMP Processes:

[00124] The CMP process for Composition R of Table R was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, a back pressure of 0 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Composition R was stirred thoroughly before and during its use.

[00125] When employed according to the process of Table R, Composition R provides a Pt removal rate of 334 A/min and a BPSG removal rate of 26 A/min, demonstrating a Pt:BPSG selectivity of 13:1.

Composition S

[00126] Other Pt polishing compositions (such as "Composition S") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, hydrochloric acid (HCl), ammonium chloride (NH₄Cl), and DI water. One example of component concentrations for Composition S is set forth below in Table XIX.

Composition S Component ConcentrationTable XIX Typical Compositions

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Hydrochloric acid	0.1 mol/1 kg
Ammonium Chloride	0.1 mol/1 kg
DI Water	Remaining weight amount to obtain final desired amount of Composition S

pH Ranges

[00127] Composition S typically has a pH range from about 1 to about 2 and, favorably, a pH of about 1.4.

Preparation

[00128] Generally, Composition S is prepared by adding the alumina abrasive (such as

CR-30) to a container of DI water, then adding the hydrochloric acid, and then adding the ammonium chloride (NH_4Cl). Composition S is advantageously stirred continuously within the container during at least the composition preparation.

CMP Process

[00129] An example of the mixing ratio, process, pH and removal rate for Composition S is set forth in Table S.

Mixing Ratio, Process and Removal Rate

Table S

Mixing Ratio	Process	pH	Pt Removal Rate (A/min)
2 wt % Alpha-Alumina Abrasive	4/0/200/18/70	1.4	310
0.1 mol/l kg Hydrochloric acid			
0.1 mol/l kg Ammonium Chloride			
DI Water			

[00130] The CMP process set forth in Table S was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 70 ml/min. Composition S was stirred thoroughly before and during its use.

[00131] When employed according to the process set forth in Table S, Composition S provides a Pt removal rate of 310 A/min.

Composition T

[00132] Other platinum polishing compositions (such as "Composition T") pursuant to some embodiments of the present invention comprise an alumina (alpha-, gamma-, or both) abrasive, hydroxylamine (HDA), and DI water. It is believed that the caustic HDA serves as a mild reducing agent. An example of component concentrations for Composition T is set forth below in Table XX.

Composition T Component ConcentrationTable XX: Typical Composition T

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
Hydroxylamine	0.1 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition T

pH Ranges

[00133] Composition T typically has a pH range from about 8 to about 9 and advantageously a pH of about 8.5.

Preparation

[00134] Generally, Composition T is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and then adding the hydroxylamine. Composition T is advantageously stirred continuously within the container during the composition preparation.

CMP Process

[00135] An example of the mixing ratio, process, pH, removal rates and selectivity for Composition T is set forth below in Table T.

Mixing Ratio, Process, pH, Removal Rates and SelectivityTable T

Mixing Ratio	Process	pH	Removal Rate (A/min) Pt	Removal Rate (A/min) BPSG	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasive	4/0/50/51/150	8.5	209	432	1:2
0.1 mol/kg Hydroxylamine					
DI water					

[00136] In the example set forth in Table T, the CMP process was carried out using an IPEC 472 polisher and employing a down force pressure of 4 psi, a back pressure of 0 psi, a table speed of 50 rpm, a carrier speed 51 rpm, and a composition flow rate of 150 ml/min. An IC-1000 k-grooved pad was used as the polishing pad on the primary platen of the polisher, and a Polytex pad was used as buff pad on the secondary platen of the polisher. Composition T was stirred thoroughly before and during its use.

[00137] When employed according to the process of Table T, Composition T provides a Pt removal rate of 209 A/min and a BPSG removal rate of 432 A/min, demonstrating a Pt:BPSG selectivity of 1:2.

Composition U

[00138] Other preferred Platinum polishing compositions (such as "Composition U") pursuant to the present invention comprise an alumina abrasive (alpha-, gamma-, or both), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), and DI water. It is believed that the hydroxylamine hydrochloride serves as an oxidizing agent. One example of component concentrations for Composition U is set forth below in Table XXI.

Composition U Component Concentration

Table XXI: Typical Composition U

Component	Component Concentration
Alpha-Alumina Abrasive (CR-30)	2 wt %
$\text{NH}_2\text{OH}\cdot\text{HCl}$	0.1 mol/l kg
DI Water	Remaining weight amount to obtain final desired amount of Composition U

pH Ranges

[00139] Composition U typically has a pH range from about 3.5 to about 4.5 and favorably a pH of about 4.

Preparation

[00140] Generally, Composition U is prepared by adding the alumina abrasive (such as CR-30) to a container of DI water and then adding the hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$). Composition U is advantageously stirred continuously within the container during at least the composition preparation.

CMP Process

[00141] An example of the mixing ratio, process, removal rate and selectivity for Composition U is set forth in Table U below.

Mixing Ratio, Process, pH, Removal Rates and SelectivityTable U

Mixing Ratio	Process	pH	Pt Removal Rate (A/min)	Removal Rate (A/min) BPSG	Pt: BPSG Selectivity
2 wt % Alpha-Alumina Abrasive	2/0/200/18/150	4	393	70	5.6:1
0.1 mol/kg $\text{NH}_2\text{OH}\cdot\text{HCl}$					
DI water					

[00142] The CMP process set forth in Table U was carried out using an IPEC 576 polisher with a Thomas West XY pad and employing a down force pressure of 2 psi, a back pressure of 0 psi, a table or platen speed of 200 rpm, a carrier speed of 18 rpm, and a composition flow rate of 150 ml/min. Composition U is advantageously stirred thoroughly before and during its use.

[00143] When employed according to the process of Table U, Composition U provides a Pt removal rate of 393A/min and a BPSG removal rate of 70 A/min, demonstrating a Pt:BPSG selectivity of approximately 5.6:1.

[00144] Those skilled in the art will appreciate that, given the present disclosure, modifications may be made to the invention without departing from the spirit of the inventive concept described herein. Therefore, it is not intended that the scope of the invention be limited to the specific embodiments illustrated and described.

CLAIMS

1. A composition for polishing a substrate surface having at least one feature thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof, comprising:
periodic acid and an abrasive in a combined amount sufficient to render the substrate surface substantially planar upon chemical-mechanical polishing thereof.
2. The composition of claim 1, wherein periodic acid is in an amount from about 0.05 to about 0.3 moles/kilogram.
3. The composition of claim 1, wherein periodic acid is in an amount from about 0.075 to about 0.175 moles/kilogram.
4. The composition of claim 1, wherein the abrasive is in an amount from about 0.2 to about 6 weight percent.
5. The composition of claim 1, wherein the abrasive is in an amount from about 0.2 to about 4 weight percent.
6. The composition of claim 1, further comprising a pH-adjusting agent selected from a group consisting of a quaternary amine, an inorganic base, or any combination thereof.
7. The composition of claim 6, wherein the pH-adjusting agent comprises an agent selected from a group consisting of tetramethylammonium hydroxide, ammonium hydroxide, potassium hydroxide, sodium hydroxide, or any combination thereof.
8. The composition of claim 1, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range of from about pH 5 to about pH 10.

9. The composition of claim 1, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 1 to about pH 4.

10. The composition of claim 1, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 2 to about pH 3.

11. The composition of claim 1, further comprising a suspension agent.

12. The composition of claim 11, wherein the suspension agent comprises an agent is selected from a group consisting of an organic acid, a surfactant, another abrasive, and ethyl carbonate.

13. The composition of claim 1, wherein the abrasive comprises an abrasive having a Mohs hardness number of greater than about 6.5.

14. The composition of claim 1, wherein the abrasive comprises an abrasive selected from a group consisting of alumina, silica, zirconia, spinel, zirconium nitride, carbide, and any combination thereof.

15. The composition of any of claims 1 through 11, wherein the abrasive comprises alumina.

16. The composition of any of claims 1 through 11, wherein the feature comprises a material selected from a group consisting of Ir, IrO₂, Pt, and any combination thereof.

17. The composition of claim 1, wherein said combined amount is sufficient to provide the substrate surface at a WWNU of less than about 12%.

18. The composition of claim 1, wherein said combined amount is sufficient to provide the substrate surface at a WTWNU of less than about 5%.

19. A composition for polishing a substrate surface having at least one feature thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof, comprising:

periodic acid in an amount from about 0.05 to about 0.3 moles/kilogram; and
an abrasive in an amount from about 0.2 to about 6 weight percent.

20. The composition of claim 19, wherein the amount of periodic acid is from about 0.075 to about 0.175 moles/kilogram.

21. The composition of claim 19, wherein the amount of the abrasive is from about 0.2 to about 4 weight percent.

22. The composition of claim 19, further comprising a pH-adjusting agent selected from a group consisting of a quaternary amine, an inorganic base, or any combination thereof.

23. The composition of claim 22, wherein the pH-adjusting agent comprises an agent selected from a group consisting of tetramethylammonium hydroxide, ammonium hydroxide, potassium hydroxide, sodium hydroxide, or any combination thereof.

24. The composition of claim 19, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range of from about pH 5 to about pH 10.

25. The composition of claim 19, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 1 to about pH 4.

26. The composition of claim 19, further comprising a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 2 to about pH 3.

27. The composition of claim 19, further comprising a suspension agent.
28. The composition of claim 27, wherein the suspension agent comprises an agent selected from a group consisting of an organic acid, a surfactant, another abrasive, and ethyl carbonate.
29. The composition of claim 19, wherein the abrasive comprises an abrasive having a Mohs hardness number of greater than about 6.5.
30. The composition of claim 19, wherein the abrasive comprises an abrasive selected from a group consisting of alumina, silica, zirconia, spinel, zirconium nitride, carbide, and any combination thereof.
31. The composition of any of claims 19 through 27, wherein the abrasive comprises alumina.
32. The composition of any of claims 19 through 27, wherein the feature comprises a material selected from a group consisting of Ir, IrO₂, Pt, and any combination thereof.
33. The composition of claim 19, wherein said composition is sufficient to render the substrate surface substantially planar upon chemical-mechanical polishing thereof.
34. The composition of claim 19, wherein said composition is sufficient to provide the substrate surface at a WWNU of less than about 12% upon chemical-mechanical polishing thereof.
35. The composition of claim 19, wherein said composition is sufficient to provide the substrate surface at a WTWNU of less than about 5% upon chemical-mechanical polishing thereof.

36. A method of polishing a substrate surface having at least one feature thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof, comprising:

providing a composition, the composition comprising periodic acid and an abrasive in a combined amount sufficient to render the substrate surface substantially planar upon chemical-mechanical polishing thereof; and

chemical-mechanical polishing the substrate surface with the composition.

37. The method of claim 36, wherein periodic acid is in an amount from about 0.05 to about 0.3 moles/kilogram.

38. The method of claim 36, wherein periodic acid is in an amount from about 0.075 to about 0.175 moles/kilogram.

39. The method of claim 36, wherein the abrasive is in an amount from about 0.2 to about 6 weight percent.

40. The method of claim 36, wherein the abrasive is in an amount from about 0.2 to about 4 weight percent.

41. The method of claim 36, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent selected from a group consisting of a quaternary amine, an inorganic base, or any combination thereof.

42. The method of claim 41, wherein the pH-adjusting agent comprises an agent selected from a group consisting of tetramethylammonium hydroxide, ammonium hydroxide, potassium hydroxide, sodium hydroxide, or any combination thereof.

43. The method of claim 36, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range of from about pH 5 to about pH 10.

44. The method of claim 36, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 1 to about pH 4.

45. The method of claim 36, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 2 to about pH 3.

46. The method of claim 36, wherein said providing comprises providing a composition that further comprises a suspension agent.

47. The method of claim 46, wherein the suspension agent comprises an agent selected from a group consisting of an organic acid, a surfactant, another abrasive, and ethyl carbonate.

48. The method of claim 36, wherein the abrasive comprises an abrasive having a Mohs hardness number of greater than about 6.5.

49. The method of claim 36, wherein the abrasive comprises an abrasive selected from a group consisting of alumina, silica, zirconia, spinel, zirconium nitride, carbide, and any combination thereof.

50. The method of any of claims 36 through 46, wherein the abrasive comprises alumina.

51. The method of any of claims 36 through 46, wherein the feature comprises a material selected from a group consisting of Ir, IrO₂, Pt, and any combination thereof.

52. The method of claim 36, wherein said chemical-mechanical polishing is sufficient to render the substrate surface substantially planar.

53. The method of claim 36, wherein said chemical-mechanical polishing is sufficient to provide the substrate surface at a WWNU of less than about 12%.

54. The method of claim 36, wherein said chemical-mechanical polishing is sufficient to provide the substrate surface at a WTWNU of less than about 5%.

55. A method of polishing a substrate surface having at least one feature thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof, comprising:

providing a composition, the composition comprising periodic acid in an amount from about 0.05 to about 0.3 moles/kilogram and an abrasive in an amount from about 0.2 to about 6 weight percent; and

chemical-mechanical polishing the substrate surface with the composition.

56. The method of claim 55, wherein the amount of periodic acid is from about 0.075 to about 0.175 moles/kilogram.

57. The method of claim 55, wherein the amount of abrasive is from about 0.2 to about 4 weight percent.

58. The method of claim 55, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent selected from a group consisting of a quaternary amine, an inorganic base, or any combination thereof.

59. The method of claim 58, wherein the pH-adjusting agent comprises an agent selected from a group consisting of tetramethylammonium hydroxide, ammonium hydroxide, potassium hydroxide, sodium hydroxide, or any combination thereof.

60. The method of claim 55, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range of from about pH 5 to about pH 10.

61. The method of claim 55, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 1 to about pH 4.

62. The method of claim 55, wherein said providing comprises providing a composition that further comprises a pH-adjusting agent in an amount sufficient for a pH level of the composition to be in a range from about pH 2 to about pH 3.

63. The method of claim 55, wherein said providing comprises providing a composition that further comprises a suspension agent.

64. The method of claim 63, wherein the suspension agent comprises an agent selected from a group consisting of an organic acid, a surfactant, another abrasive, and ethyl carbonate.

65. The method of claim 55, wherein the abrasive comprises an abrasive having a Mohs hardness number of greater than about 6.5.

66. The method of claim 55, wherein the abrasive comprises an abrasive selected from a group consisting of alumina, silica, zirconia, spinel, zirconium nitride, carbide, and any combination thereof.

67. The method of any of claims 55 through 63, wherein the abrasive comprises alumina.

68. The method of any of claims 55 through 63, wherein the feature comprises a material selected from a group consisting of Ir, IrO₂, Pt, and any combination thereof.

69. The method of claim 55, wherein said chemical-mechanical polishing is sufficient to render the substrate surface substantially planar.

70. The method of claim 55, wherein said chemical-mechanical polishing is sufficient to provide the substrate surface at a WWNU of less than about 12%.

71. The method of claim 55, wherein said chemical-mechanical polishing is sufficient to provide the substrate surface at a WTWNU of less than about 5%.

72. A substrate having a surface with at least one feature thereon comprising a noble metal, a noble metal alloy, a noble metal oxide, or any combination thereof, said substrate produced by the method of any one of claims 36 and 55.

73. The substrate of claim 72, wherein the surface thereof is substantially planar.

74. The substrate of claim 72, wherein the substrate surface has a WWNU of less than about 12%.

75. The substate of claim 72, wherein the surface thereof has a WTWNU of less than about 5%.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/27330

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09G1/02 C23F3/06 C09K3/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09G C23F C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 332 831 B1 (OWAKI TOSHIKI ET AL) 25 December 2001 (2001-12-25) the whole document	1

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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